Determination of Trace Metal Impurities in Semiconductor Grade Phosphoric Acid by High Sensitivity Reaction Cell ICP-MS

Application

Semiconductor

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Abstract

Metallic impurities in semiconductor grade phosphoric acid were determined by a newly developed high sensitivity reaction cell inductively coupled plasma mass spectrometer (ICP-MS). The Agilent 7500cs ICP-MS, which features an Octopole Reaction System (ORS) for interference removal, was used to analyze 85% (w/w) phosphoric acid (H_3PO_4) following a 100-fold dilution, for elements specified in SEMI C36-0301, Specifications and Guidelines for Phosphoric Acid. By pressurizing the ORS with simple gases, hydrogen and helium, all plasma and matrix based polyatomics that interfere with the measurement of elements such as Ca, Fe, Ti, Co, Ni, Cu, and Zn are easily attenuated while maintaining excellent sensitivity for all other elements in non-gas mode. The ShieldTorch System (STS) and new ion lens assembly used in the Agilent 7500cs provides excellent signal/background resulting in exceptional detection limits for all elements (0.06–28 ppt range). Excellent spike recovery data at the 50 ppt level in 0.85% H_3PO_4 further highlights the suitability and accuracy of the Agilent 7500cs for the determination of SEMI required elements at trace levels in H_3PO_4.

Introduction

Contamination control in semiconductor processing is increasingly important as device critical dimensions (CD) continue to shrink. Particulate contamination, which can lead to device defects, needs to be minimized at each of the manufacturing stages. Impurity levels present in the various process chemicals are controlled and monitored closely. Phosphoric acid (H_3PO_4) is used for wet chemical etching of silicon nitride films (Si_3N_4). It is critical that the wafer surface is not contaminated by any metallic impurities present in the acid, as micro-contamination accounts for over 50% of the yield losses in IC manufacturing [1]. In order to minimize this risk, many incoming chemicals, including H_3PO_4, are analyzed for their chemical purity and the etching baths are sampled regularly.

Interference Removal

Plasma and matrix-based polyatomic overlaps on critical elements present specific analytical problems for conventional quadrupole ICP-MS for many semiconductor applications. The introduction of the ShieldTorch interface with the original HP 4500 in 1994 revolutionized the use of ICP-MS in the semiconductor industry, resulting in the acceptance of cool plasma as the standard technique for ultratrace analysis. This was due to the unique capability of cool plasma to remove plasma-based polyatomic interferences on the key elements K

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(ArH), Ca (Ar), and Fe (ArO) [2]. However, with the introduction of the high-sensitivity 7500cs reaction cell ICP-MS, which has been specifically designed for semiconductor applications, analysts now have the flexibility to attenuate matrix interferences using reaction cell technology. The 7500cs also features a new extraction lens design which reduces Easily Ionized Elements (EIE) background equivalent concentrations (BECs) close to cool plasma levels, under normal plasma conditions. All applications can be performed at 1500W forward power with the added advantage of Agilent cool plasma performance still being available for those users who have exisiting and proven methodology based on cool plasma.

The analyst has complete flexibility over choice of analysis mode: normal, He, H_2, or cool plasma. The 7500cs ChemStation software allows data to be acquired automatically in multiple modes, with the results combined into a single report.

Analysis of H_3PO_4

Phosphoric acid is a high viscosity acid (65cP viscosity at 20 °C); therefore, a 100 times dilution in ultrapure water is required prior to analysis. Also, since H_3PO_4 cannot be purified by distillation, metal impurity levels are normally above 1 ppb. Maximum allowable levels (ppb), as stated in the SEMI C36-0301 Specifications and Guidelines for Phosphoric Acid document, appear in Table 3.

The analysis of H_3PO_4 by ICP-MS is challenging for conventional systems because of the presence of various molecular species that interfere with many key semiconductor elements. In addition to the plasma-based interferences on ^{39}K ($^{38}Ar^1H$), ^{40}Ca (^{40}Ar), and ^{56}Fe ($^{40}Ar^{16}O$), the analysis of Ti, Co, Ni, Cu, and Zn in H_3PO_4 is made more challenging by the presence of the matrix-based polyatomics (shown in Table 1), which interfere with some important elements.

Table 1. Phosphorus Polyatomic Interferences on Ti, Co, Ni, Cu, and Zn

Polyatomic ions	Mass	Analyte
PNH	46	Ti
PO	47	Ti
POH	48	Ti
POH_2	49	Ti
PCO, PN_2	59	Co
PN_2H	60	Ni
PO_2, P_2H	63	Cu
PO_2H	64	Zn
PO_2	65	Cu
PO_2H	66	Zn

Even though these plasma and matrix-based interferences can be minimized by the Agilent 7500s ICP-MS operating in cool plasma mode, the BECs for the semiconductor critical elements Ti, Zn, and Cu are greatly improved by using the 7500cs ORS ICP-MS, as seen in the data presented in Table 2.

Table 2. Comparison of ORS-Based Performance (7500cs) with Non-reaction Cell Performance (7500s)

Analyte	7500cs - ORS ICP-MS mode	BEC ppt	7500s non-cell ICP-MS mode	BEC ppt
Ti (46)	Helium	36	Normal	170
Co (59)	Helium	0.47	Cool	0.4
Ni (60)	Helium	21	Cool	23.7
Cu (65)	Helium	3.9	Cool*	2700*
Zn (66)	Helium	9.6	Normal	36

*Copper measurements determined on mass 63

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Instrumentation

The instrument used in this application was an Agilent 7500cs ICP-MS equipped with an ORS, ShieldTorch System (STS), and PFA Inert Kit. The PFA Inert Kit (Agilent part number G3139A #301) consists of a PFA-100 high efficiency, self-aspirating micro flow nebulizer, 35-mm PFA Pure-Cap end cap, 35-mm PFA spray chamber, 2.0-mm O-ring free platinum injector, and precision quartz torch. A low flow nebulizer and platinum interface cones were used to prevent deterioration of the interface by the acid.

Argon and matrix-based polyatomic ions on key elements like Ca, Fe, Ti, Co, Ni, Cu, and Zn were eliminated by pressurizing the Octopole Reaction cell with H_2 or He. Several methods of interference removal are provided with the ORS [3]. Using He as a cell gas promotes collisional dissociation and energy discrimination (this allows the ORS to discriminate between analyte ions and larger polyatomic ions). Efficiency in collision mode is greatly improved by Agilent's STS, which produces ions with very low and uniform ion energies. Hydrogen induces ion-molecular reactions used for the efficient removal of the intense peaks due to plasma-based species, CO^+, N_2^+, Ar^+, ArO^+, and Ar_2^+.

The 7500cs ChemStation software controls all instrument operations including tuning and data acquisition — automatically combining different acquisition modes, data analysis, and reporting.

Methodology

Sample Preparation

Because of the high viscosity of H_3PO_4 (2.4 times higher than sulfuric acid), samples were diluted 100 times in ultrapure water prior to analysis. Analyses were performed using the method of standard additions (MSA). Calibration curves were prepared at concentrations ranging from 20 to 500 ng/L (ppt). A single MSA curve was established and converted into an external calibration curve, thereby eliminating the need to spike each subsequent sample to be analyzed. Once an external calibration curve is established from the MSA curve, all other sample concentrations can be determined against it. No internal standards were used in this study to minimize the risk of sample contamination. Following quantitation, H_3PO_4 samples were spiked at a level of 50 ppt (ng/L) to assess the accuracy of the measurement.

ICP-MS Analysis

The sample was self-aspirated at an uptake rate of 100 µL/min. To demonstrate the range of operation modes available, data were acquired using both ORS mode and cool plasma conditions to eliminate matrix interferences. Comparative data for the two modes are shown in Table 4, page 4. Data for all SEMI specified analytes is given except for Si and Sb: Sb is present at high levels in H_3PO_4, which significantly increases BEC and detection limits (DL) values, and accurate spike recovery at the 50 ppt level is not possible. Further method development is required for the accurate measurement of Si in H_3PO_4 at ultratrace levels by ICP-MS.

Results and Discussion

The results shown in Table 3 show 3-sigma DL (ppt), BECs (ppt) and spike recovery data (%) for a standard suite of semiconductor elements in 0.85% H_3PO_4. Note the excellent performance for elements such as K, Ca, Ti, Co, Ni, Cu, and Zn, which suffer plasma and matrix-generated interferences. The results for Ti, Co, Ni, Zn, and Cu particularly highlight the effectiveness of the 7500cs for removing the phosphorus based interferences (see Table 1, page 2), allowing the direct analysis of these elements in H_3PO_4. The Cr and Fe values suggest that there were some impurities present in the sample, and the level of Sb was not reported as it was above the top calibration standard. Results for all other elements were well below the maximum allowable levels (ppb) stated in the SEMI Specifications and Guidelines for Phosphoric Acid document (C36-0301), and all recoveries were within the SEMI acceptable range of 75%–125%.

Table 4 shows the comparison between the data for EIE acquired at 1500W and the cool plasma (600W) results. The new ion lens system on the 7500cs eliminates the extraction of these EIE from the interface region when high RF power is used. This

Table 3.   DL (3 sigma) and BECs and Spike Recoveries of SEMI Specified Elements in 0.85% H_3PO_4

Element (mass)	Plasma power	H_2 Gas flow (mL/min)	He Gas flow (mL/min)	DL 3 sigma, n = 10 (ppt)	BEC (ppt)	*SEMI Grade 3 spec - max level (ppb)	Spike recovery (%) 50 ppt spike (*200 ppt)
Li (7)	Normal	4.5	–	0.58	0.44	10	99*
B (11)	Normal	–	–	28	110	50	79*
Na (23)	Normal	4.5	–	3.4	34	250	97*
Mg (24)	Normal	4.5	–	2.3	15	50	99*
Al (27)	Normal	4.5	–	3.4	7.0	50	100*
K (39)	Normal	4.5	–	3.0	19	150	101*
Ca (40)	Normal	5.0	–	5.7	24	150	92
Ti (46)	Normal	–	4.5	10	36	50	104
V (51)	Normal	–	4.5	0.50	0.31	–	97
Cr (52)**	Normal	–	4.5	10**	55**	50	113
Mn (55)	Normal	5.0	–	0.80	3.4	50	98
Fe (56)**	Normal	5.0	–	22**	180**	100	95
Co (59)	Normal	–	4.5	0.40	0.47	50	98
Ni (60)	Normal	–	4.5	4.5	21	50	90
Cu (65)	Normal	–	4.5	1.7	3.9	50	96
Zn (66)	Normal	–	4.5	5.3	9.6	50	90
As (75)	Normal	–	4.5	5.3	9.5	50	93
Sr (88)	Normal	–	–	0.07	0.13	10	100
Cd (111)	Normal	–	–	2.2	5.0	50	107
Sb (121)	Normal	–	–	–	>500	1000	–
Ba (138)	Normal	–	–	0.20	0.45	50	102
Au (197)	Normal	–	–	0.70	1.8	50	99
Pb (208)	Normal	–	–	1.4	7.0	50	101

Normal plasma power = 1500W, *Maximum acceptable levels in undiluted phosphoric acid, **Suggests impurities in H_3PO_4.

reduces backgrounds, allowing the ultratrace measurement of Li, Na, Mg, Al, and K even at high-plasma power (1500W). Though BEC and DL values obtained at high power for some EIE are slightly higher than with cool plasma, they compare favorably with previously reported values obtained in 1%w/w H_3PO_4 using reaction cell ICP-MS [4].

Representative calibration curves are given in Figure 1. Excellent correlation coefficients were obtained for all elements.

Table 4.   Comparison of DL (3 sigma) and BECs for EIEs in 0.85% H_3PO_4 Acquired Using Cool and Normal Plasma Power. H_2 was Added at a Flow Rate of 4.5 mL/min

Element (mass)	DL (ppt)		BEC (ppt)	
	Cool	Normal + H_2	Cool	Normal + H_2
Li (7)	0.10	0.58	0.070	0.44
Na (23)	6.7	3.4	28	34
Mg (24)	2.8	2.3	13	15
Al (27)	1.1	3.4	4.1	7.0
K (39)	1.3	3.0	2.4	19

Detection limits were calculated using three times the standard deviation (n = 3) of the raw counts of the H_3PO_4 blank divided by the slope of the calibration curve. The reported DLs are good and are dependent upon the trace metal content in the blank. This provides an opportunity for even further improvement upon the reported values should higher purity H_3PO_4 become available. All DLs are in the range 0.1–28 ppt (ng/L) in the 0.85% H_3PO_4.

Ti — Mass 46, Step 4, Units ppt, Count/CPS(Y) count/CPS unweighted

Lv.	Conc.	Count/CPS	RSD %
1	0.00	18.50	P 14.60
2	20.00	30.00	P 16.00
3	50.00	45.60	P 8.16
4	100.00	68.40	P 11.40
* 5	200.00	121.00	P 3.46
* 6	500.00	261.00	P 2.01

Curve Fit: Y=aX+[blank]+bkg
r = 0.9988   Conc.= 3.638E+001 ppt
Y = 5.094E-001*X +1.853E+001 +bkg
bkg = 0.000E+000

Cu — Mass 65, Step 4, Units ppt, Count/CPS(Y) count/CPS unweighted

Lv.	Conc.	Count/CPS	RSD %
1	0.00	31.20	P 13.10
2	20.00	237.00	P 9.94
3	50.00	508.00	P 2.43
4	100.00	949.00	P 5.76
* 5	200.00	1860.00	P 3.09
* 6	500.00	4750.00	P 1.37

Curve Fit: Y=aX+[blank]+bkg
r = 0.9996   Conc.= 3.364E+000 ppt
Y = 9.279E+000*X +3.121E+001 +bkg
bkg = 0.000E+000

Zn — Mass 66, Step 4, Units ppt, Count/CPS(Y) count/CPS unweighted

Lv.	Conc.	Count/CPS	RSD %
1	0.00	26.00	P 27.40
2	20.00	91.20	P 2.79
3	50.00	195.00	P 7.02
4	100.00	331.00	P 3.18
* 5	200.00	666.00	P 2.50
* 6	500.00	1620.00	P 2.02

Curve Fit: Y=aX+[blank]+bkg
r = 0.9982   Conc.= 8.315E+000 ppt
Y = 3.122E+000*X +2.596E+001 +bkg
bkg = 0.000E+000

B — Mass 11, Step 2, Units ppt, Count/CPS(Y) count/CPS unweighted

Lv.	Conc.	Count/CPS	RSD %
1	0.00	866.00	P 7.88
* 2	20.00	1040.00	P 9.71
3	50.00	1080.00	P 7.03
4	100.00	1490.00	P 3.98
5	200.00	2050.00	P 9.18
* 6	500.00	4190.00	P 8.04

Curve Fit: Y=aX+[blank]+bkg
r = 0.9963   Conc.= 1.471E+002 ppt
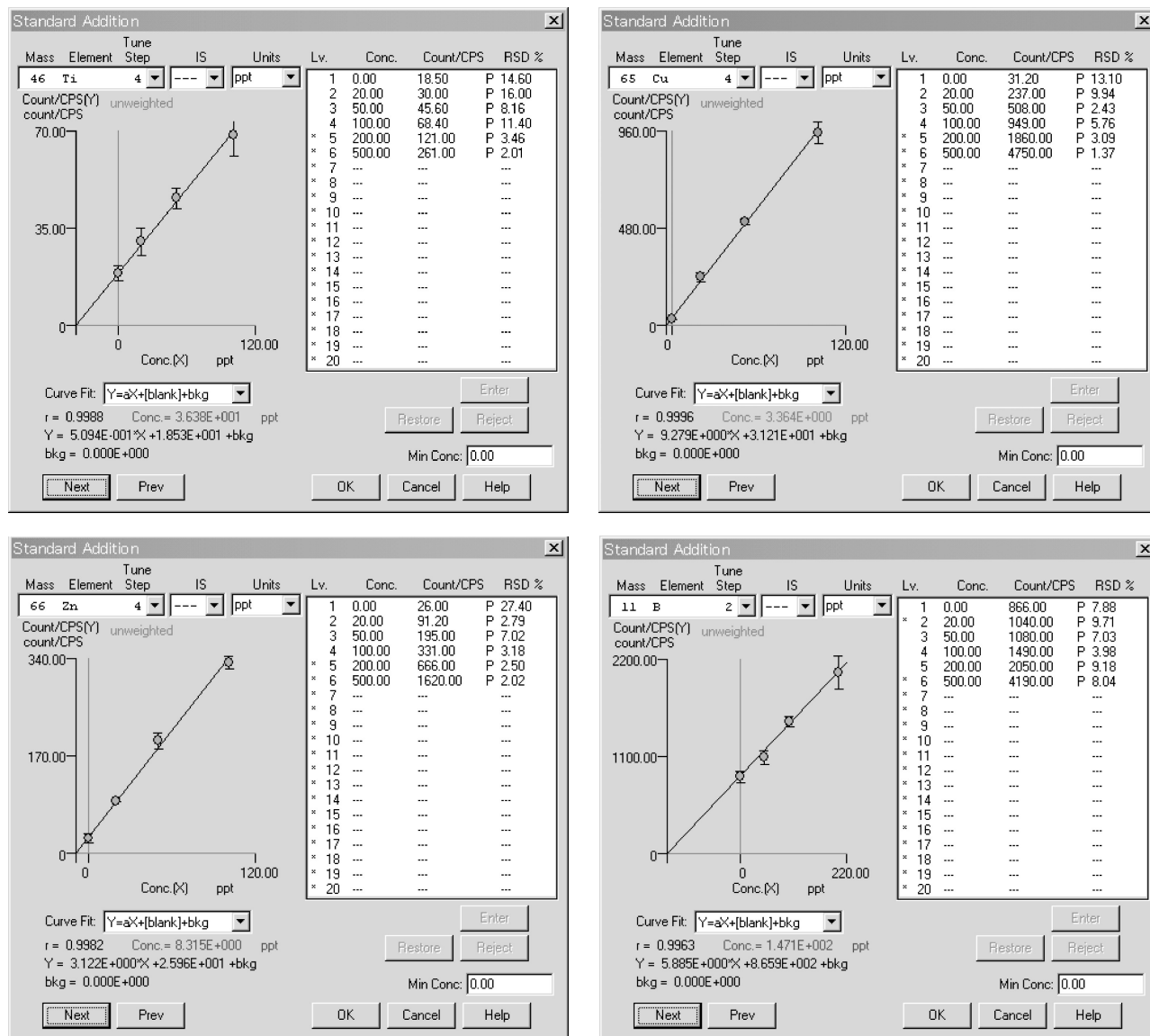Y = 5.885E+000*X +8.659E+002 +bkg
bkg = 0.000E+000

Figure 1.   Representative calibration curves for Ti, Cu, Zn, and B obtained using method of standard addition (Blank, 20, 50, 100, 200, and 500 ppt).

A short-term stability study was performed by adding a 100 ppt standard into the 0.85% H_3PO_4 and analyzing the spiked sample over a 3-hour period. Instrument stability over this period was excellent, with %RSD values typically less than 15%. A stability plot of representative elements is shown in Figure 2.
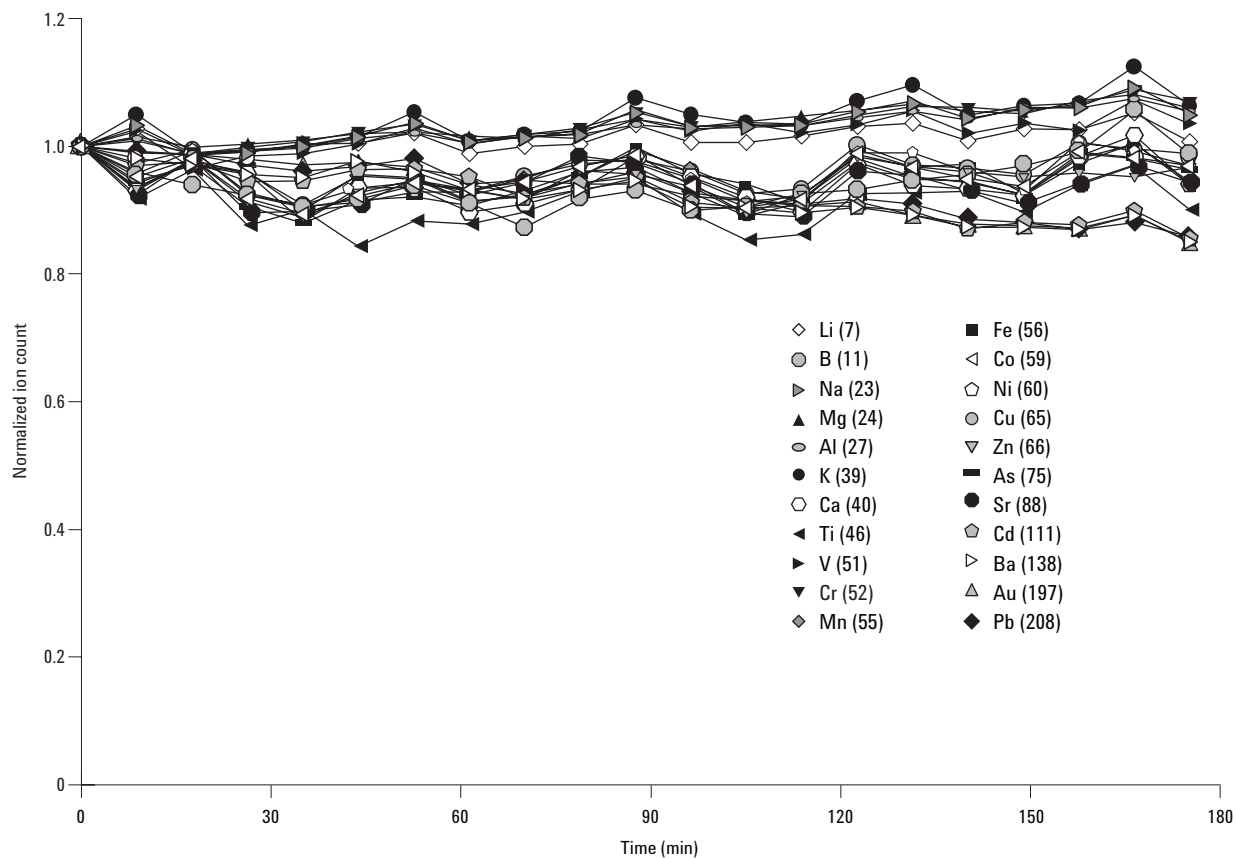

Figure 2. Analysis of 100 ppt multi-element standard spiked into 0.85% H_3PO_4 measured repeatedly over a 3-hour period. Analysis time per sample including 60 s of sample uptake was 185 s (0.33 s integration time, except Ti - 1 s, three replicate measurements).

Conclusions

A newly developed high sensitivity reaction cell ICP-MS was used to analyze 85% (w/w) H_3PO_4 following a 100-fold dilution for elements specified in SEMI Specifications and Guidelines for Phosphoric Acid. The Agilent 7500cs features a new-design ion-lens system for high ion transmission and an ORS cell for interference removal. By pressurizing the cell with simple gases like hydrogen and helium, argon and phosphate-based polyatomics are removed, allowing the direct, ppt-level measurement of Ti, Cu, and Zn in H_3PO_4.

The new extraction lens design also reduces the BECs for the EIEs to close to cool plasma levels even at 1500W or 1600W forward power (normal plasma). All applications can be performed at normal power with the added advantage of Agilent cool plasma performance still being available, if required. Even though BEC and DL values obtained at high power for EIEs are slightly higher than with cool plasma, they are appropriate for the measurement of trace contaminants in H_3PO_4 and they compare favorably with previously reported values obtained in 1%w/w H_3PO_4 using reaction cell ICP-MS [4].

The DL, BEC, spike recovery and stability data presented in the application note highlight the suitability and accuracy of the Agilent 7500cs ICP-MS to determine ppt level impurities in H_3PO_4 for all of the important SEMI specified elements. All analytes were measured directly on mass, in a single analytical run with automatic switching of cell and plasma parameters. A typical total analysis time for this application is 4 minutes. All data is automatically combined into a single report.

Samples were analyzed using the MSA. Only the first sample is spiked with the calibration standards and a MSA regression is generated, which is then converted to an external calibration curve. This method eliminates the need to spike all subsequent samples aiding sample throughput.

References

1. Werner Kern. Handbook of Semiconductor Wafer Cleaning Technology. William Andrew Publishing; 1993. Chap 2, section 2.3, p. 8.

2. K. Sakata, and K. Kawabata. Reduction of Fundamental Polyatomic Ions in Inductively Coupled Plasma Mass Spectrometry. Spectrochim. Acta 1994; (49B): 1027.

3. N. Yamada, J. Takahashi and K. Sakata. The Effects of Cell-gas Impurities and Kinetic Energy Discrimination in an Octopole Collision Cell ICP-MS under Non-Thermalized Conditions. JAAS 2002; 17: 1213–1222.

4. K. Kawabata, Y. Kishi, and R. Thomas. The Benefits of Dynamic Reaction Cell ICP-MS Technology to Determine Ultratrace Metal Contamination Levels in High-Purity Phosphoric and Sulfuric Acid. Spectroscopy 2003 Jan; 18 (1): 16–31.

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